

Experimental Evidence for Quantum Interference and Vibrationally Induced Decoherence in Single-Molecule Junctions

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We analyze quantum interference and decoherence effects in single-molecule junctions both experimentally and theoretically by means of the mechanically controlled break junction technique and density-functional theory. We consider the case where interference is provided by overlapping quasi-degenerate states. Decoherence mechanisms arising from the electronic-vibrational coupling strongly affect the electrical current flowing through a single-molecule contact and can be controlled by temperature variation. Our findings underline the all-important relevance of vibrations for understanding charge transport through molecular junctions.

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Charge transport through single-molecule junctions [1, 2] is a quantum mechanical process. It was first treated as a purely electronic problem, combining transport concepts and quantum chemical calculations. Similarly, early experiments focused on the correlation between chemical structure and transport properties [3–6]. Inspired by the related process of electron transfer in molecules, which is strongly dominated by vibration-assisted electronic phenomena, it became evident that a purely electronic picture is also inadequate in single-molecule transport [7–9].

Vibrations may appear as vibrational sidepeaks to electronic transitions [10–14], and constitute a source for non-linear phenomena [15, 16] and bistabilities [17, 18]. In addition, vibrations may also provide a strong decoherence mechanism in molecular junctions where electron transport is governed by destructive interference effects [19].

In a purely electronic picture, destructive interference is a built-in property of many molecules commonly used in molecular junctions [20–24]. It occurs when the current is carried by quasi-degenerate electronic states (orbitals) which, *e.g.*, differ in their spatial symmetry (see Fig. 1 a). In analogy to a double-slit experiment, these states provide different pathways (which are not necessarily spatially separated) for the electrons to tunnel through the molecular junction. Although their individual contribution to the current would be substantial, their phase-correct sum current can be very small (if the broadened levels overlap sufficiently, as sketched in Fig. 1 a).

Interaction with vibrations may change this result significantly [19]. As a rule, electronic states couple very specifically to vibrations, in particular a different electronic-vibrational coupling of the quasi-degenerate

levels is expected. Consequently, destructive interference between the involved pathways is quenched, which affects the electron transmission, *i.e.* the electrical current. In

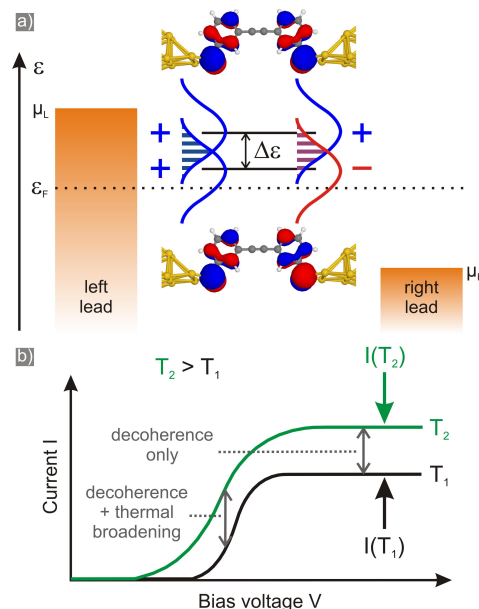


FIG. 1: (Color online) Panel (a): We consider a scenario where two molecular orbitals are close in energy ($\Delta\epsilon$) and sufficiently broadened such that they strongly overlap. We call them quasi-degenerate. In this case, interference becomes important. In particular, when two such orbitals differ in their spatial symmetry, destructive interference results in a suppression of the current flowing through the orbital pair. Panel (b): In the resonant tunneling model including vibrationally induced decoherence [19], the current plateaus $I(T)$ are sensitive to vibrational excitation, which can be tuned by temperature. $I(T)$ is therefore a suitable observable to investigate vibrationally induced decoherence.

more general terms, which-path information is provided by coupling to the vibrations.

In an experiment, vibrations are inherent to any molecular junction, in particular at room temperature. Their influence can be controlled by systematically varying the temperature of the junction. When starting at low temperatures T , the influence of vibrations is minimal. With increasing T decoherence will continuously be tuned on *via* enhanced vibrational excitation, leading to an effectively increased electronic-vibrational interaction. Hence, for systems which exhibit destructive interference, the expectation is an increase of the electrical current with increasing T (cf. Fig. 1 b).

The scope of this paper is to analyze vibrationally induced decoherence in single-molecule junctions experimentally, accompanied by a detailed analysis of the molecular systems using density-functional theory (DFT). To this end, we have selected several molecules out of a class of rather typical molecular wires (conjugated, thiol-/pyridine-endcapped) [5, 25, 26]. The employed systems are depicted in Fig. 2. In contrast to the molecule in the previous theoretical studies [19], which had a built-in L \leftrightarrow R symmetry, we used molecules with a reduced symmetry: in particular, molecule **2** has two different endgroups in meta- and para-position (cf. Ref. [27]). In molecule **3**, the conjugated system is intersected in the center by a σ bond, and the left and right conjugated subunits are spatially twisted by approximately 75° with respect to each other (leading to electronic states localized either on the right or on the left end of the molecular rod). The study of systems **1–3** shows that L \leftrightarrow R symmetric molecules are only a special case of a more general class of systems, where quasi-degenerate states close to the Fermi energy generate vibration-sensitive interferences. For a specific molecule, the existence of such states also depends on the molecule-lead linker group. For example, molecule **4** has the full L \leftrightarrow R symmetry. However, due to its pyridine anchor groups, the resulting quasi-degenerate states are located remote from the Fermi energy and, thus, do not contribute to the current. Therefore, this system provides a counter-example where it is expected that the considered mechanism does not affect the electrical current.

We use the mechanically controlled break junction technique at cryogenic vacuum conditions to establish single-molecule junctions at atomically sharp, free-standing gold tips, and record current-voltage-characteristics (I - V 's). Details of the method including sample processing can be found elsewhere [3, 28]. We restricted our investigation to a temperature range of 8 to 40 K, where the geometric structure of the junction is stable under temperature sweeps (see below). Above 40 K, the junctions exhibit hysteresis and/or irreversibilities of the I - V 's.

Typical I - V curves are sketched in Fig. 1 b. The current flowing through a molecular junction is suppressed,

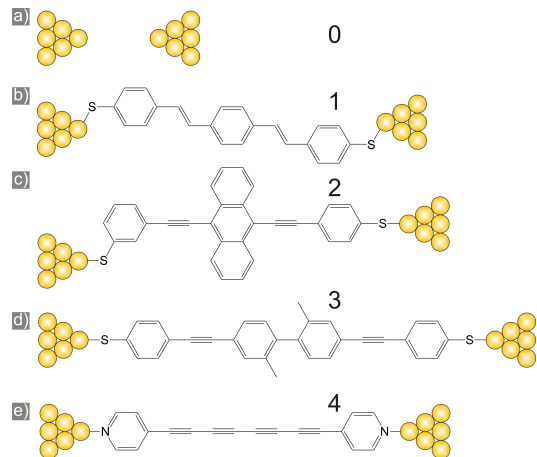


FIG. 2: (Color online) Overview of the molecular systems investigated. Panel (a): Atomically sharp gold electrodes (blind experiment). Panel (b) – (d): Molecules **1** – **3** with thiol anchoring groups. Panel (e): Molecule **4** with pyridine anchoring groups.

as long as the voltage V is sufficiently low that the electronic levels of the junction are located outside the energy window defined by the two chemical potentials μ_L and μ_R in the left and the right leads, respectively ($V = (\mu_L - \mu_R)/e$). This range of bias voltages defines the non-resonant transport regime. If one or more electronic levels are located within the bias window $[\mu_L, \mu_R]$, resonant transport processes occur.

The transition is indicated by a step-like increase of the current level that remains almost constant for larger voltages unless another electronic state enters the bias window. This plateau has often a slightly positive slope, as quasi continuously new vibrational side channels are added, which can hardly be resolved [14]. It is on this first plateau in $I(V)$ where the analysis of the temperature dependence of the current level is carried out. It is particularly suited because in the resonant tunneling model (without vibrations) it is not affected by thermal broadening, *i.e.* the temperature dependence of the Fermi distribution function in the leads.

The temperature dependence of the electrical current flowing through a single-molecule junction has been considered before [7, 29–32]. However, the experimental phenomenology presented in these papers is different and the previous discussion focused on effects that occur at much larger temperatures ($\gtrsim 150$ K) and/or in the non-resonant transport regime.

Before discussing the temperature dependence of single-molecule junctions, we present data on a blind experiment using a pair of gold electrodes which was treated only with solvent. The addressed question is whether the setup is sufficiently stable with respect to temperature variations. A temperature sweep from 10 K to 33 K does not show significant variations of the tunneling current,

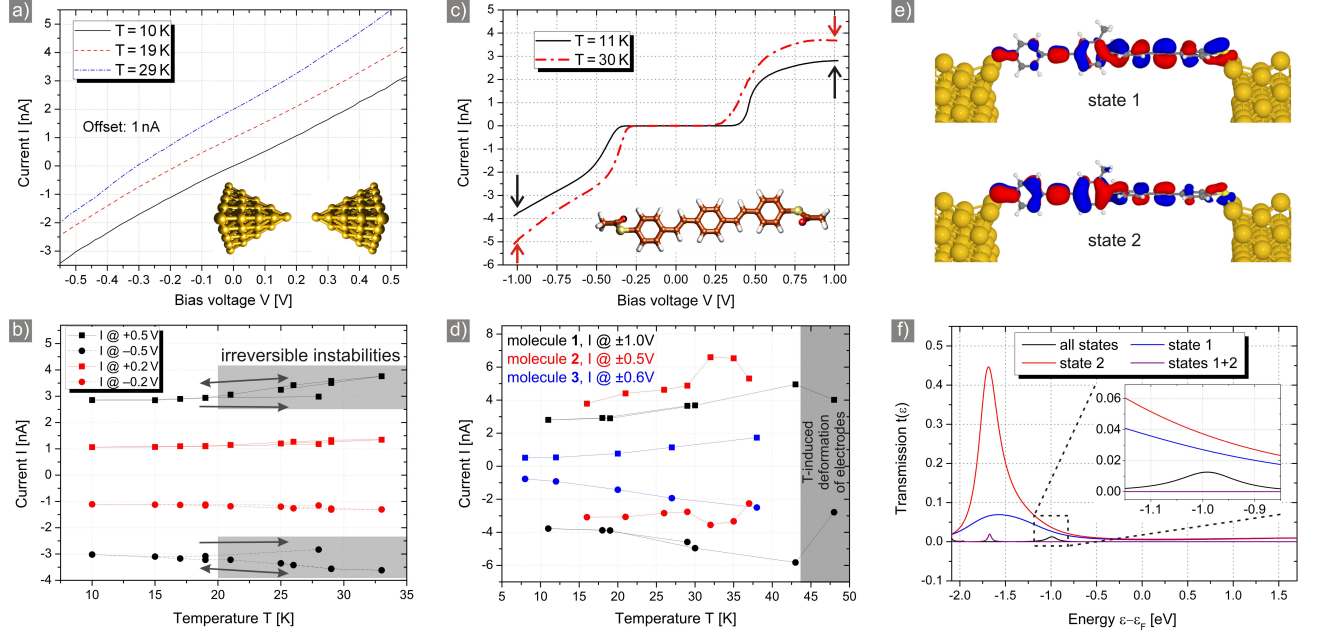


FIG. 3: (Color online) I - V - and I - T -characteristics for gold electrodes [blind experiment, panel (a) and (b)], for molecule **1** [panel (c)] and for molecules **1–3** [panel (d)], respectively. The temperature-dependent current $I(T)$ recorded at the first plateau is the key observation indicating vibrationally induced decoherence. Panel (e): Molecular junction **3** provides a pair of quasi-degenerate states located next to the Fermi level. The corresponding wave functions differ in symmetry. Panel (f): Transmission functions for electron transport through molecular junction **3**. The individual (broadened) peaks associated with the quasi-degenerate states 1 and 2 at $\epsilon - \epsilon_F \simeq -1.7$ eV are relatively strong, but their phase-correct transmission (states 1 + 2) shows only a very small peak at this energy due to destructive interference. When including all states this peak is shifted to -1.0 eV below ϵ_F .

if the bias is low ($\lesssim 0.2$ V, see Fig. 3 a-b). At higher bias though, irreversible drifts are observed at $T > 22$ K. This small instability occurs presumably due to atomic rearrangements at high electric fields in the tip region. This behavior is quite common in the absence of a bridging molecule, but we learnt from many experiments that a bridging molecule stabilizes the junction and allows for stable conditions up to ≈ 1.5 V at low T [4]. We therefore conclude that in the temperature range considered the electrode pair provides a stable distance.

We now investigate the temperature dependence of the current flowing through a single-molecule junction. As a first example, we present data obtained with molecule **1** (see Fig. 3 c). The I - V -characteristics show a typical behavior: a fairly symmetric blockade region up to ± 0.43 V at 11 K and subsequently a step-like transition to a current plateau which, however, is less symmetric. When measuring the very same junction at $T = 30$ K two changes are evident. First, the blockade region is slightly reduced to ± 0.35 V. Second, the current level taken at the first plateau of the I - V -characteristics is significantly increased. This becomes evident in Fig. 3 d, where the current level at ± 1.0 V (cf. arrows in Fig. 3 c) is plotted versus temperature. In contrast to the blind experiment, a clear increase of the current by about 65% is observed, which remains reversible up to $T \approx 40$ K. Again, at higher

temperatures, we observe a drift. This phenomenology is qualitatively reproduced for several samples.

We continue by seeking more examples for this effect, and investigate molecules **2** and **3**. For all thiol-endcapped molecular wires (**1–3**), we observe qualitatively and reproducibly the same effect (see Fig. 3 d): an increase of the current with temperature that is intrinsic to the molecular junction, as inferred by the blind experiment.

To rationalize the underlying mechanism, we analyze theoretically the transmission of molecular junction **3**, which shows the most pronounced temperature effect in the experiment. To this end, we employ a model based on first-principles electronic structure calculations [19, 33] and obtain the respective transmission function within Landauer theory [1]. It is depicted by the solid black line in Fig. 3 f. Peaks in this transmission function indicate that electrons can tunnel resonantly through the junction. Accordingly, the first plateau in the current is related to the peak that is closest to the Fermi level ϵ_F . For our example, this is the small peak at $\epsilon - \epsilon_F \simeq -1$ eV (highlighted in the inset of this figure). Analysis shows that this peak results predominantly from electron transport processes through two electronic states. The orbitals corresponding to these two states are shown in Fig. 3 e. They represent symmetric and antisymmetric combina-

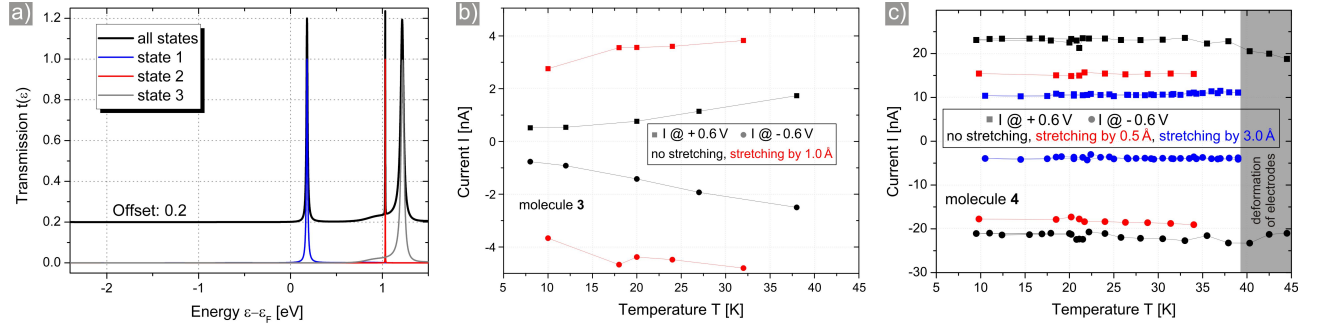


FIG. 4: (Color online) Panel (a): Transmission function for electronic transport through molecular junction **4**. The black curve is the superposition of the three individual contributions (red, blue and grey). In this molecular junction the states close to the Fermi energy are not quasi-degenerate and no sign for destructive interference occurs. Panel (b) and (c): I - V - and I - T -characteristics upon stretching of molecular junctions **3** and **4**, respectively.

tions of molecular orbitals localised in the left and the right part of the molecular bridge. If we take into account electron transport through just one of these states, we obtain transmission functions, which are depicted by the solid red and blue lines in Fig. 3f. Both states are located relatively close in energy ($\Delta\epsilon \sim 0.02$ eV), and are strongly broadened (~ 0.5 eV). This is what we termed quasi-degenerate states (cf. Fig. 1a). The broadening is a result of the strong coupling between the molecular bridge and the leads mediated by the sulfur endgroups. The results in Fig. 3f shows that electron transport through these states is governed by pronounced destructive quantum interference effects [19], which reduce their relatively large individual transmission function to a small peak at $\epsilon - \epsilon_F \cong -1$ eV. It is worth mentioning that the occurrence of quasi-degenerate states is quite general and can be found in many molecular wires, irrespective of $L \leftrightarrow R$ symmetry. Even the choice of electronically very different linker groups (cf. molecule **2**) does not suppress the effect.

As we have shown recently [19], electronic-vibrational coupling can strongly quench such interference effects, leading to substantially larger electrical currents. This quenching is enhanced the more strongly the vibrational degrees of freedom are excited. A normal mode analysis of molecular junction **3** shows a broad distribution of vibrational modes located on the molecular bridge. Their frequencies range from 1.2 meV to 0.4 eV, including 10 modes with a frequency lower than 10 meV (approximately $2k_B T_{\max}$). Among these modes is the torsion (3.7 meV) around the central σ bond which is particular important for the coupling of the left and right conjugated subunit, forming states 1 and 2 in Fig. 3e. Increasing the temperature in the leads from 8 K to $T_{\max} = 40$ K leads to a substantial excitation of these modes and, *via* the thus enhanced vibrationally induced decoherence, to a larger current level. This correlates well with the experimental findings (see Fig. 3d).

In order to test the correlation between a tempera-

ture dependence of the first current plateau and the appearance of quasi-degenerate states, we sought a counterexample. As the observed effect is robust even for asymmetric endgroups, we selected a completely different system: molecular wire **4**, which involves pyridine- instead of thiol-anchoring groups. The corresponding transmission function of this junction, which is depicted by the solid black line in Fig. 4a, shows a number of peaks close to the Fermi level. In contrast to molecular junction **3**, each of these peaks can be associated with a single, non-degenerate electronic state of this junction. This can be inferred by comparison to the solid red, blue and gray lines representing the transmission probability for electron transport through individual states of the junction. This analysis shows that quantum interference effects and vibrationally induced decoherence are not expected to play a dominant role for electron transport through this junction.

The experimental results confirm this prediction: the temperature dependence of the first current plateau is indeed flat for the pyridine-endcapped wire **4**, as displayed in Fig. 4c. We conclude that the comparison of various molecules reveals a clear correlation: when quasi-degenerate states are present the first current plateau rises with temperature, if not, a temperature dependence is absent. This gives convincing evidence that decoherence due to coupling to vibrations plays an important role in single-molecule charge transport.

Another independent experimental strategy to test the relevance of decoherence is to modify the coupling to the leads *via* mechanically stretching the junction. We observed in the past that for thiol-endcapped molecules an Ångström-scale stretching of the molecular bridge often resulted in an increase of current, despite the fact that the opposite behavior is observed in empty tunnel junctions. We previously assumed that this modifies the transparency by altering the sulfur-gold bonding angle. With the given model at hand, another explanation occurs: when the coupling of the two quasi-degenerate lev-

els to the leads is reduced, their mutual overlap becomes smaller and destructive interference effects are weakened. Experimentally this would result in (i) a larger current level and (ii) a reduced temperature dependence.

We can test this conjecture by observing the temperature dependence upon stretching the molecular junction. Thereby, we assume that stretching reduces the level broadening due to a smaller overlap with the metal electrodes. This was done experimentally for molecule **3** (displaying a T -dependence, see Fig. 4b) and **4** (displaying no T -dependence, see Fig. 4c). For the thiol-endcapped molecule **3** the current level *increases* upon stretching (in line with previous observations and prediction (i)) by a factor of 2-3. This can be interpreted as the reduction of destructive interference, but one may also invoke different explanations. For further clarification it is instructive to analyze again the temperature dependence: for molecule **3** the relative increase of current, $\Delta I(T)/I$, when changing the temperature from 8 K to 40 K is 230%. This value reduces to 35% upon stretching, in line with (ii). We assign this reduced temperature dependence to a reduction of the level broadening and a reduced overlap between the identified quasi-degenerate states (see Fig. 1a).

Again, the situation is different for molecule **4**, which has no quasi-degenerate levels close to ϵ_F : using the same experimental protocol, the current level is slightly *reduced* upon stretching, since interference plays a minor role (see Fig. 4c). The insensitivity to temperature, however, is maintained. The different response upon stretching gives additional evidence to the picture that resonant electron transport through the thiol-endcapped molecular junctions **1–3** is governed by destructive interference of quasi-degenerate levels.

To conclude, our experimental studies reveal that the electrical current flowing through a single-molecule junction in the resonant transport regime exhibits an intrinsic temperature dependence. By analyzing four molecules experimentally and theoretically, this temperature effect can be correlated with the presence of quasi-degenerate electronic states which give rise to destructive quantum interference. When increasing the temperature, the low-frequency modes of the junction are excited, which induces decoherence and thus increases the current. We expect this phenomenon to be of importance for a broad class of molecular wires where quasi-degenerate levels are close to the Fermi energy, irrespective of symmetry conditions. Its impact on the transport characteristics will be significantly more pronounced at room temperature. The effect underscores that vibrations play a crucial and non-trivial role in electronic transport through molecular junctions.

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